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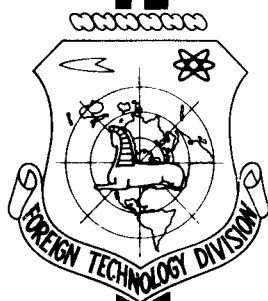
TRANSLATION

THE FORMATION OF HYDRAZINE BY THE ACTION OF
 γ -RADIATION ON SOLID AND LIQUID AMMONIA

By

Yu. A. Sorokin and S. Ya. Pshezhetskiy

FOREIGN TECHNOLOGY DIVISION



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THE FORMATION OF HYDRAZINE BY THE ACTION OF
Y-RADIATION ON SOLID AND LIQUID AMMONIA

Yu. A. Sorokin and S. Ya. Pshetskiy

As is known, a change in the state of a substance is noticeably manifested in a number of cases during radiochemical reactions. The differences between the gas phase and the liquid phase are well-known, but the differences between the liquid and solid phases are less known. However, it is difficult to compare the available, limited data for the processes in these phases, for example, for radiolysis of hydrocarbons, because these investigations have been carried out for the most part at different temperatures. Therefore, the effects observed could be associated both with the differences in the properties of the liquid and solid phases and with the difference in the rates of these or other stages due to temperature differences.

Evidently the effect of the state on the occurrence of radiochemical processes is interesting to investigate first of all at a small temperature difference. It is also important that the reactions are not complex and that the observable effects can be correlated with a change in the conditions for particular primary or secondary elementary processes. The formation of hydrazine on irradiation of ammonia is such a reaction.

We investigated the formation of hydrazine in liquid and solid ammonia

^{gamma} was studied
exposed to ~~gamma~~-radiation. Certain data are given ^{on} ~~in this report that are interesting~~
~~from the point of view of the characteristics of the effect of the state of the~~
process.

Ammonia was irradiated in quartz ampules with a Co^{60} -radiation source with an activity of $2 \cdot 10^4$ curie. The radiation intensity varied between 25 and 790 r/sec. The magnitude of the absorbed energy was determined by a ferrous sulfate dosimeter. The radiation period was from 10 to 104 minutes.

After irradiation ammonia was removed by evaporation. Hydrazine was determined by the photocalorimetric method in a solution of p-dimethylaminobenzaldehyde hydrochloride. The accuracy of determining the hydrazine by this method was of the order of 10^{-1} mg/ml.

The dependence of hydrazine yield on the temperature is shown in Fig. 1.

The hydrazine yield increases with a drop in temperature in the liquid phase. However, the hydrazine yield falls on passing through the solidification point of ammonia (-78°); in the solid phase the yield is smaller approximately by one order of magnitude than in the liquid phase. Therefore, the transition from the liquid to the solid state leads to a jump-like change in the hydrazine yield. The temperature dependence of the hydrazine yield in the liquid phase corresponds to an activation energy of 3-4 kcal/mole.

The observed phase effect can be explained by the change in conditions for the formation of NH_2 radicals.

Apparently the main reactions leading to the formation of hydrazine are the following:

1. $\text{NH}_3 \rightleftharpoons \begin{cases} \text{NH}_2 + \text{H} \\ \text{NH} + \text{H}_2 \end{cases}$
2. $\text{NH}_2 + \text{NH}_2 \rightarrow \text{N}_2\text{H}_4$
3. $\text{NH} + \text{NH}_2 \rightarrow \text{N}_2\text{H}_4$

The concentration of NH_2 radicals depends on the reverse recombination of hydrogen atoms with "their" NH_2 radicals. The moving away of a hydrogen atom

from "its" NH_2 radical is easier in the liquid than in the solid phase. This apparently is one of the reasons for the more efficient formation of hydrazine in the liquid phase.

If such an explanation is valid, then any hydrogen acceptor should increase the hydrazine yield. The action of the acceptor in the solid phase should be stronger than in the liquid phase, since in the liquid phase, owing to the easier "removal" of the hydrogen atoms as compared with the solid phase, the capture of hydrogen atoms by the acceptor should have a smaller effect on the yield.

We carried out the experiments with propylene as the acceptor of hydrogen atoms. The results of the experiments are shown in Figs. 2 and 3. In order to eliminate the effect of possible distortions of the solid lattice of ammonia by the molecules of the acceptor, experiments were carried out simultaneously with the addition of quantities of propane, which is not a hydrogen acceptor. We see in Fig. 2 that the yield of hydrazine increases in solid ammonia with an increasing amount of propylene.

Thus the phase effect apparently, primarily lies in the fact that the conditions for recombination of H atoms and NH_2 are changed. However, the observed effects are probably not due entirely to this cause.

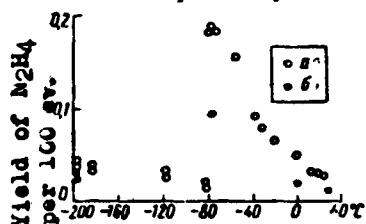


Fig. 1. Energy yield of hydrazine vs. temperature. Irradiation time 4 hr.

- a.) intensity $1.2 \cdot 10^{16}$ ev/g · sec;
- b.) intensity $4.1 \cdot 10^{16}$ ev/g · sec.

Evidently, the difference in the recombination conditions of the NH_2 radicals with the formation of hydrazine (as well as for the reaction of the NH_2 molecules) should also be of importance. The conditions in the liquid phase are apparently

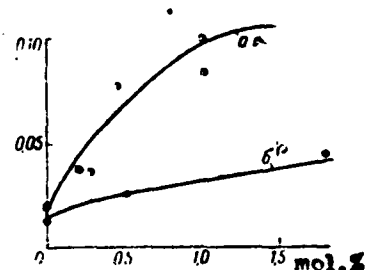


Fig. 2. Energy yield of hydrazine vs. mol. % of addition in solid phase. Intensity 200 r/sec. Irradiation time 4 hr. Temperature - 80°; a.) Propylene; b.) propane

more favorable not only for the formation of NH_2 radicals, but also for their interaction, since the mobility of these radicals is essential for their recombination. Such mobility is absent in the solid state. As certain data show, in the solid phase proper there is almost no recombination of the NH_2 radicals and even more so, almost no reaction of NH radicals with NH_3 . It is necessary to note that a lower temperature also does not promote these reactions. This follows from a comparison between the number of radicals determined by the electron paramagnetic resonance method in solid ammonium and the amount of hydrazine which was formed (Table 1).

TABLE 1

	Absorbed energy, ev/g	Number of particles per 1 g NH_3	Energy yield G, particles/100 ev
Formation of radicals	$0,37-0,39 \cdot 10^{21}$	$0,53-0,59 \cdot 10^{18}$	0,15
Formation of hydrazine	$0,35 \cdot 10^{21}$	$0,14 \cdot 10^{18}$	0,038

As the data show, the yield of hydrazine corresponds in order of magnitude to the amount of frozen radicals. This shows that at least under these conditions there is virtually no reaction in the solid phase. Apparently it proceeds during thawing of the irradiated samples when the particles acquire a certain mobility.

The negative temperature dependence of hydrazine formation in liquid ammonia can depend on various reasons. One of them could be the decomposition of hydrazine. Since with small concentrations of it the absorption of radiation by the hydrazine molecules proper is negligible in comparison with the absorption by ammonia, the decomposition of hydrazine should occur mainly as a result of the interaction with the intermediate products of the radiolysis of ammonia, for example with the NH_2 or NH radicals. Such reactions have a temperature coefficient due to the activation energy of the reaction of the radicals with the H_2H_4 molecules and, consequently, the reactions will be accelerated by a temperature rise, which will lead to a decrease in the hydrazine content.

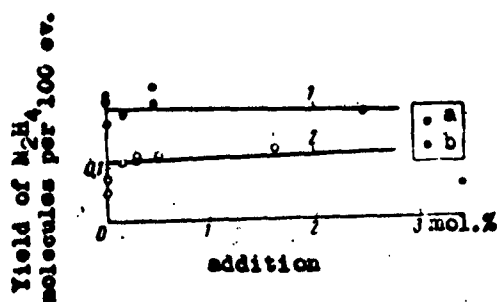


Fig. 3. Dependence of the energy yield of hydrazine on the mol. % of the addition in the liquid phase. Radiation intensity 200 r/sec. Irradiation time 4 hr. 1.) $t = -70^{\circ}$ 2.) $t = -35^{\circ}$; a.) Propylene; b.) propane

An examination shows that a combination of hydrazine-formation reactions (for example, reaction 2) with such hydrazine-decomposition reactions leads to a nonlinear dependence of the hydrazine concentration on the energy dose, and with sufficiently large energy doses the N_2H_4 concentration should acquire a steady value as a result of an equalization of its formation and decomposition rates. However, the experimental dependences (see Fig. 4) shows that deviations from linearity are still not observed in the range of the investigated doses.

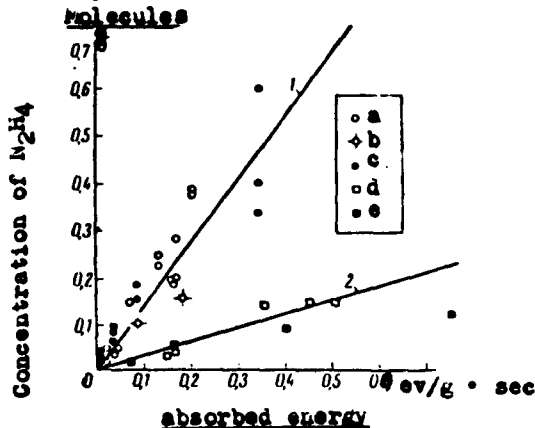


Fig. 4. Dependence of the hydrazine yield on the absorbed energy of γ -radiation. 1) liquid ammonia, $t = -75^{\circ}$; a.) radiation intensity $1.17 \cdot 10^{16}$ ev/g. sec; b.) radiation intensity $4.1 \cdot 10^{16}$ ev/g. sec; a and b, exposure is varied; c.) constant exposure, intensity is varied. 2.) solid ammonia, $t = -196^{\circ}$; d.) radiation intensity $1.17 \cdot 10^{16}$ ev/g. sec; d and e, the exposure is varied.

Another possible cause for the negative temperature dependence can be due to the accelerated diffusion of NH_2 radicals from the tracks as the temperature increases and thus the probability of recombination with the formation of N_2H_4 decreases. Such mechanism corresponds to the value of the negative effective activation energy of the order of $-3-4$ kcal/mole.

Yield values of about 0.2 molecules per 100 ev agree in order of magnitude with the value previously determined by one of us and by Ye. V. Bol'shun and I. A. Mysnikov /1/ upon irradiation of liquid ammonia by fast electrons (about

0.7 molecules per 100 ev).

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1. Ye. V. Bol'shun, S. Ye. Panzhetstiy, and I. A. Myasnikov. Collection:
The Effect of Ionizing Radiation on Inorganic and Organic Systems, Izdatel'stvo
AN SSSR, p. 184, 1958

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